Supporting Information for the Manuscript

Graphene Transforms Wide Band Gap ZnS to a Visible Light Photocatalyst. The New Role of Graphene as a Macromolecular Photosensitizer

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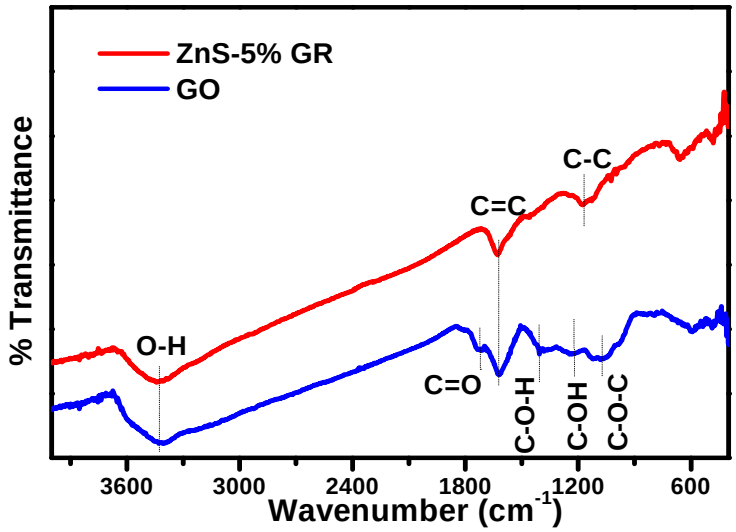

Figure S1. The Fourier transformed infrared spectra (FTIR) of the ZnS-5%GR nanocomposite and the original GO.

Note: For the bare GO, the stretching vibrations of O-H (3426 cm^{-1}), C=O (1720 cm^{-1}), C=C (1622 cm^{-1}), C-O-H (1408 cm^{-1}), C-OH (1224 cm^{-1}), and C-O-C (1057 cm^{-1}) are observed, indicating the presence of various oxygen-containing functional groups. For the ZnS-5%GR nanocomposite, the intensity of various oxygen-containing functional groups is significantly decreased, which qualitatively indicates the reduction of GO to GR after the hydrothermal treatment process. The FTIR result is in agreement with the XPS data.

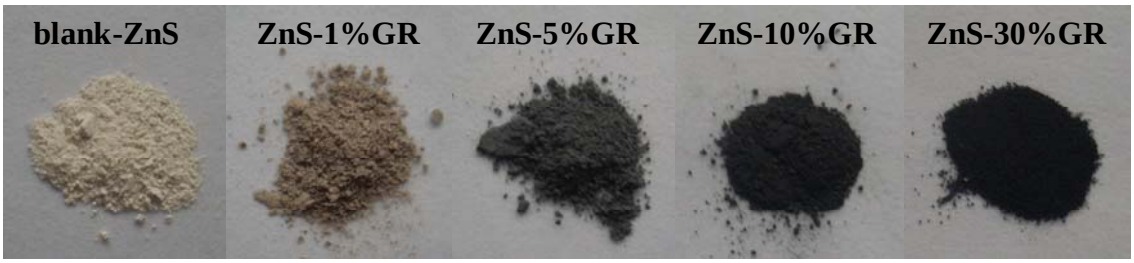

Figure S2. Photographs of the samples of blank-ZnS and ZnS-GR nanocomposites with different weight addition ratios of GR.

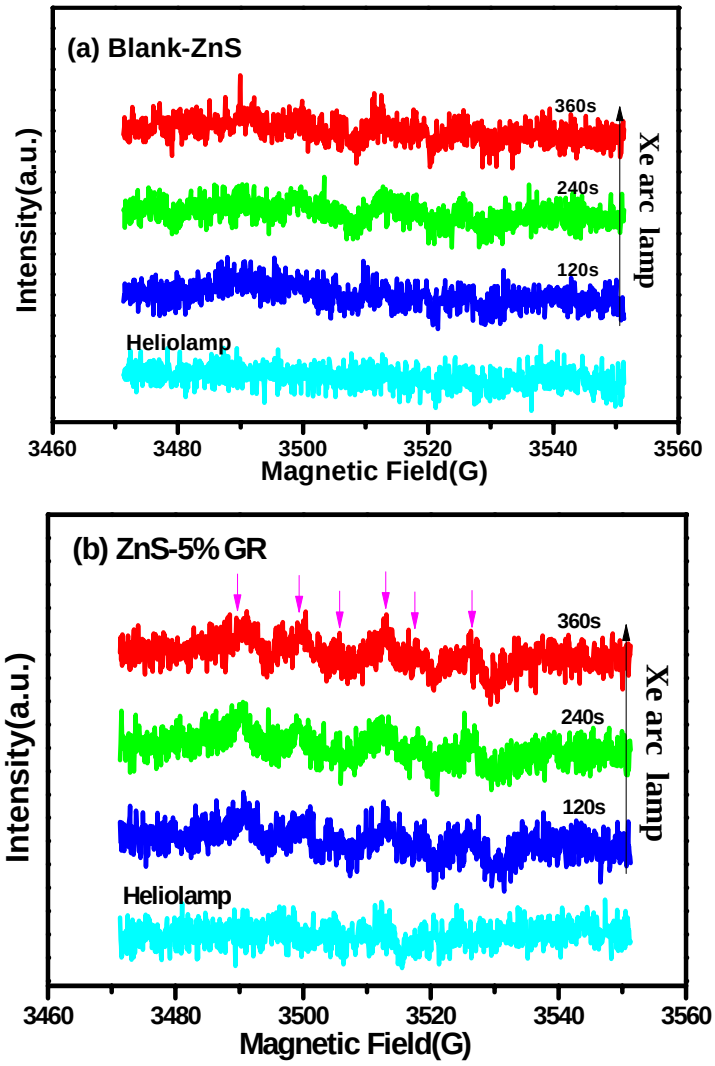

Figure S3. ESR spectra of DMPO-$O_2^{\bullet-}$ adduct in the blank-ZnS (a) and ZnS-5%GR (b) dispersion in benzotrifluoride (BTF) under the irradiation of visible light (λ>420 nm) whereas no hydroxyl radicals are detected.

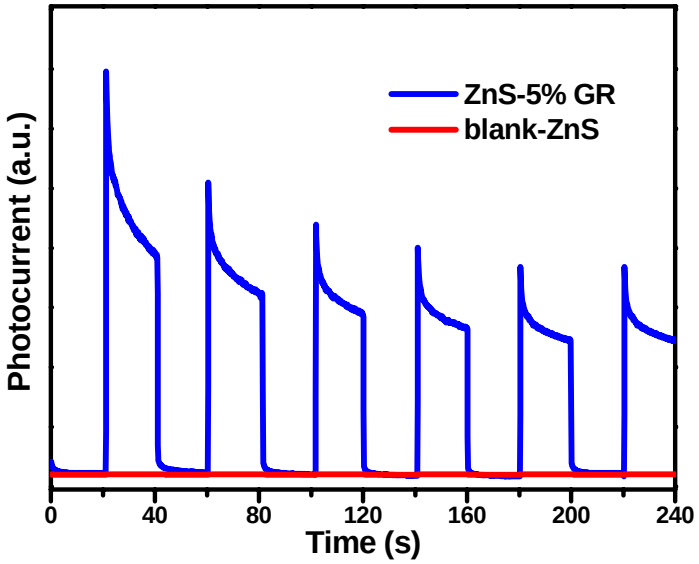

Figure S4. Photocurrent transient responses of blank-ZnS and ZnS-5%GR electrodes in a 0.2 M of Na_2SO_4 aqueous solution (pH=6.8) under visible light irradiation (λ>420 nm).

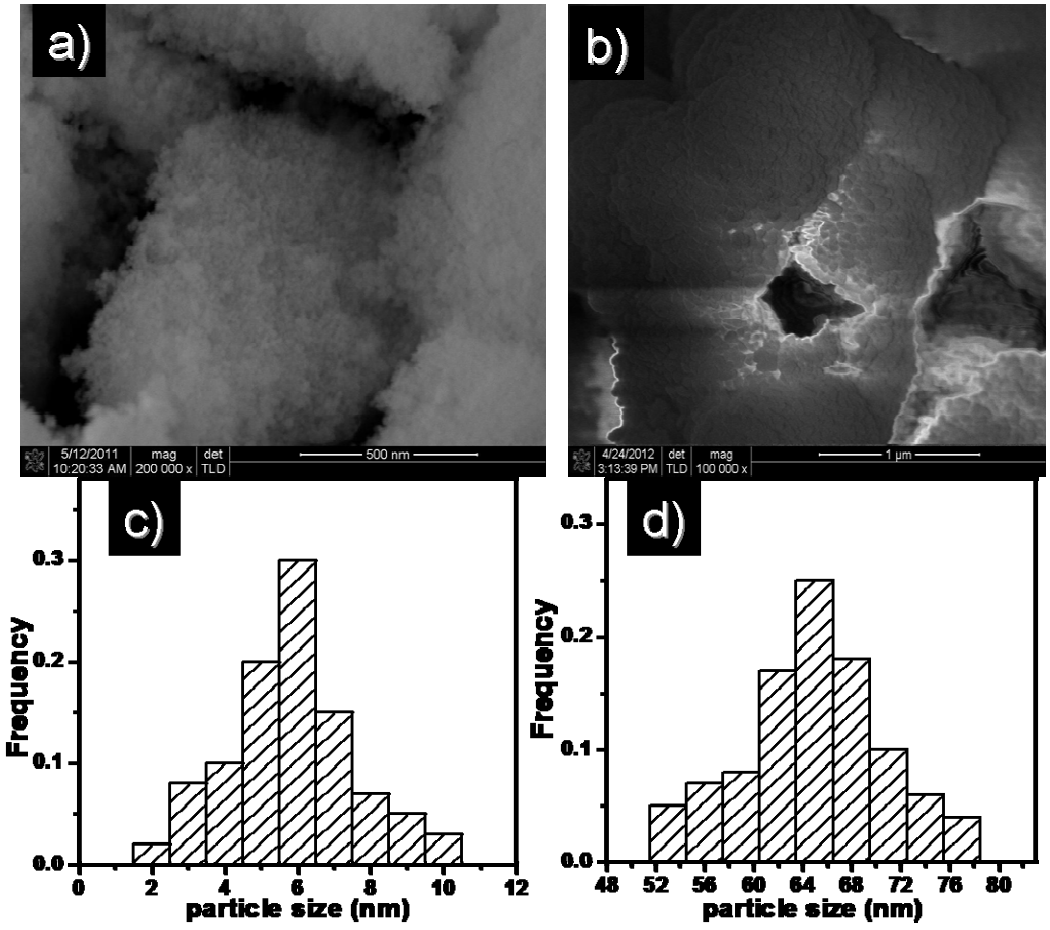

Figure S5. SEM images of blank-ZnS (a) and commercial ZnS (b); size distribution of blank-ZnS (c) and commercial ZnS (d).

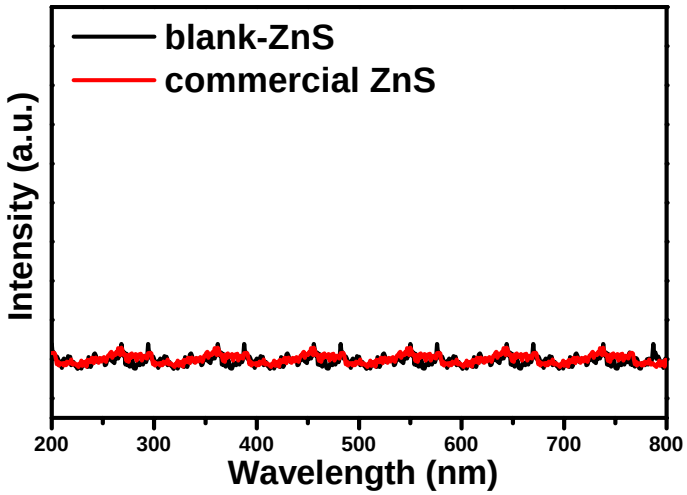

Figure S6. Photoluminescent **(**PL) spectra of blank-ZnS and commercial ZnS excited at 420 nm.

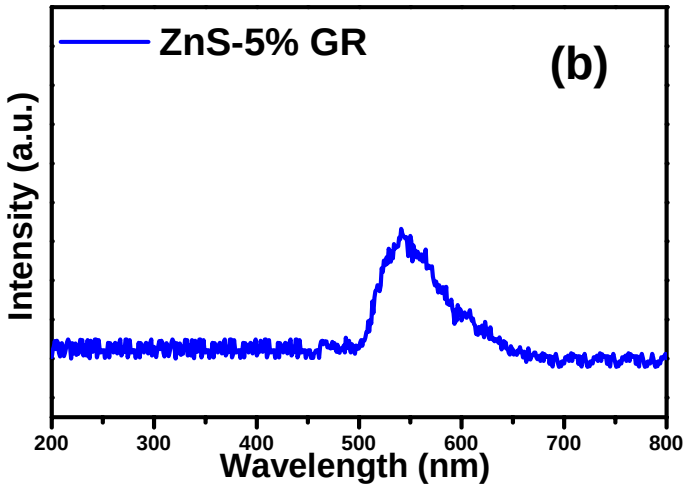

Figure S7. Photoluminescent **(**PL) spectra of ZnS-5%GR excited at 420 nm.

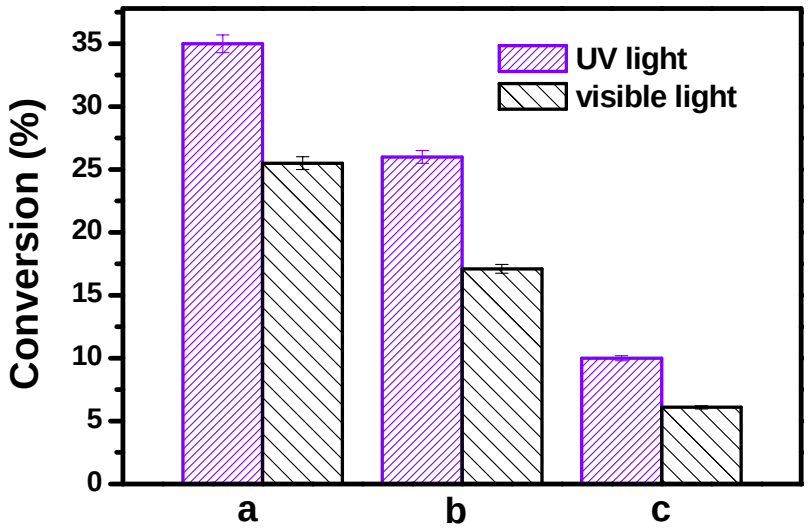

Figure S8. Photoactivity test for benzyl alcohol (a), 3-methyl-but-2-en-1-ol (b), and styrene (c) over ZnS-5%GR under UV light (λ=350±15nm) and visible light (λ>420nm) irradiation for 4 h.

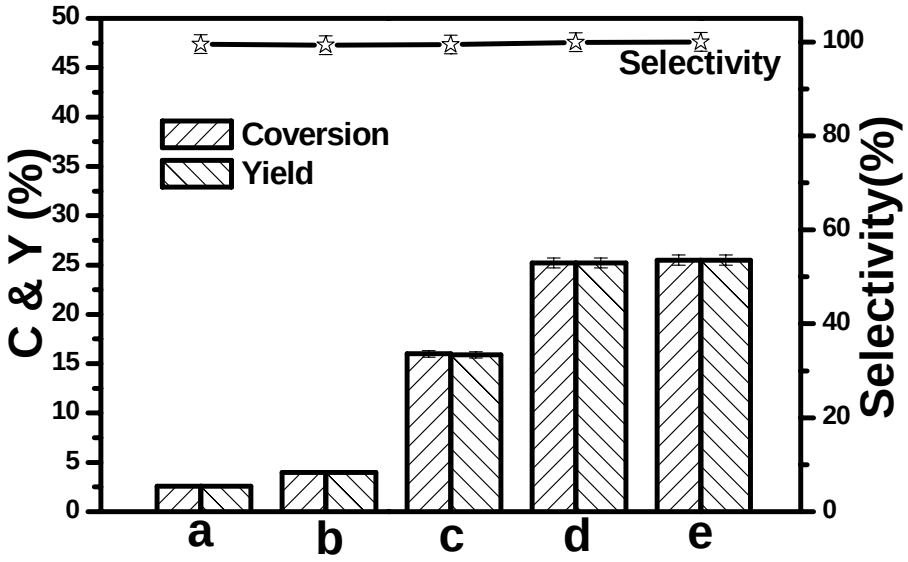

Figure S9. Results of photocatalytic selective oxidation of benzyl alcohol to benzaldehyde over ZnS-5%GR for different hydrothermal treatment times at 403 K of 0 h (a), 1 h (b), 4 h (c), 8 h (d), and 12 h (e) under visible light irradiation (λ>420nm) for 4 h.

Appendix. Synthesis of graphene oxide (GO) by a modified Hummers method

Graphene oxide (GO), the precursor of graphene (GR), was synthesized from natural graphite powder by a modified Hummers method. Typically, 2 g of graphite powder (supplied from Sinopharm Chemical Reagent Co., Ltd., China) was put into a mixture of 12 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$, and 2.5 g of P_2O_5. The solution was heated to 80 ℃ in an oil-bath kept stirring for 24 h. The mixture was then carefully diluted with 500 mL of deionized (DI) water, filtered, and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This pre-oxidized graphite was then subjected to oxidation described as follows. In a typical procedure, pre-oxidized graphite powder was added to a mixture of 120 mL of concentrated H_2SO_4 and 30 mL HNO_3 under vigorous stirring, and the solution was cold to 0 ℃. Then, 15 g of $KMnO_4$ was added gradually under stirring and the temperature of the mixture was kept to be below 20 ℃ by cooling. Successively, the mixture was stirred at room temperature for 96 h, and then diluted with 1 L of DI water in an ice bath to keep the temperature below 50 ℃ for 2 h. Shortly after the further diluted with 1 L of DI water, 20 mL of 30 % H_2O_2 was then added to the mixture and a brilliant yellow product was formed along with bubbling. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. The filter cake was then dispersed in water by a mechanical agitation. Low-speed centrifugation was done at 1000 rpm for 2 min. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproduct. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO, which exhibits the brilliant yellow color.

Appendix. AFM images and height profiles of GO:

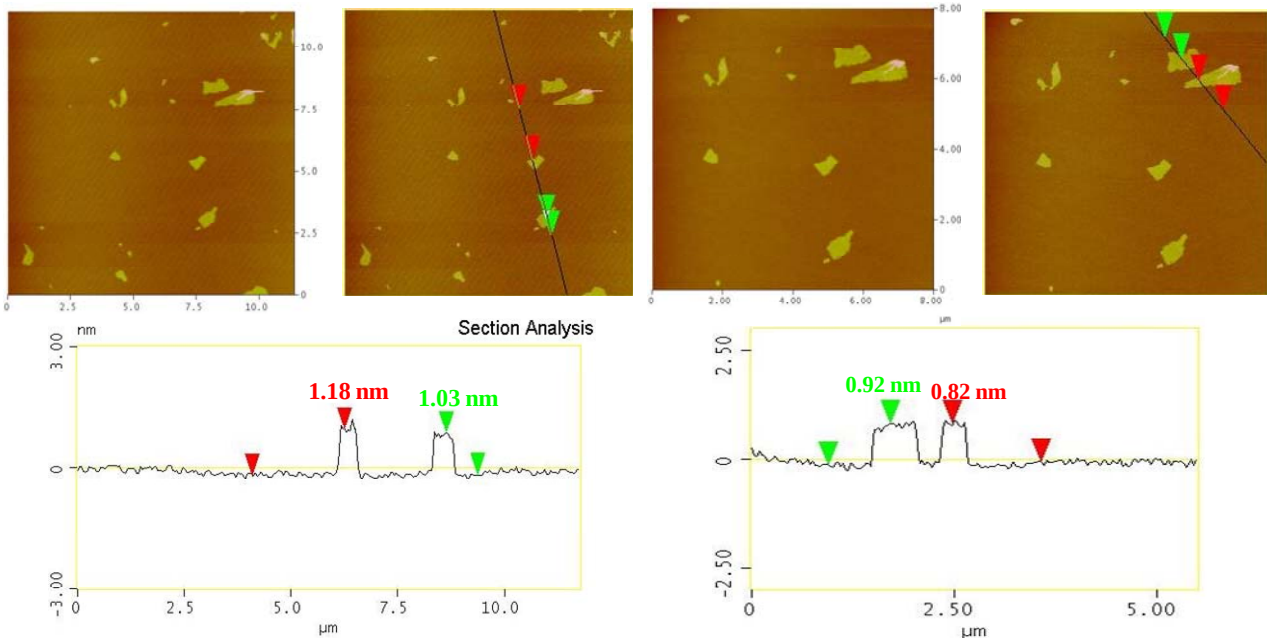

Figure S10. AFM images and height profiles of the GO sample.